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Electronic structure of $\text{Li}_{12}\text{Si}_7$

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Ab initio localized-spherical-wave calculations on crystalline $\text{Li}_{12}\text{Si}_7$ are reported. The crystal consists of two one-dimensional units, $(\text{Li}_6\text{Si}_5)_\infty$ and $(\text{Li}_{12}\text{Si}_4)_\infty$, that contain five-membered Si rings and four-membered Si stars, respectively. In the density of states the region below -5 eV is largely determined by the local ringlike and starlike arrangements of the Si atoms; above -5 eV there is a signature of delocalization of states across the subunits. Additional calculations on the separate units show that $\text{Li}_{12}\text{Si}_7$ can be described as $[\text{Li}_{12}\text{Si}_4]^{4+}[\text{Li}_6\text{Si}_5]_2^{2-}$ where the charge transfer places the Fermi energy in the gaps of the aromatic subunits. A simple molecular orbital model is presented in order to rationalize the occurrence of these gaps. A short comparison to the theoretical density of states of liquid $\text{Li}_{12}\text{Si}_7$ is also presented.

I. INTRODUCTION

The Li-Si system offers a rich variety of solid crystalline compounds. The Li-rich side of the phase diagram is well known. Crystalline compounds exist with the compositions $\text{Li}_{21}\text{Si}_5$, $\text{Li}_{13}\text{Si}_4$, $\text{Li}_{14}\text{Si}_6$, $\text{Li}_{12}\text{Si}_7$,¹⁻⁵ and, recently discovered, LiSi .⁶ Most of these compounds are similar to the Zintl phases but only LiSi conforms to the strict Zintl picture; i.e., formally one electron is donated by Li to Si and the Si^- ions form three bonds with neighboring Si ions. Note, however, that no tetrahedra are formed.

The crystal structure of $\text{Li}_{12}\text{Si}_7$ is described in Ref. 3. It consists of two basic building blocks: columns of alternately Si_5 rings and staggered Li_5 rings with an extra Li in the center of the latter (Li_6Si_5 unit) and intertwined chains of Si_4 stars in a plane with a “cloud” of Li around them ($\text{Li}_{12}\text{Si}_4$ unit). There are twice as many “rings” as there are “stars”: $(\text{Li}_6\text{Si}_5)_2\text{Li}_{12}\text{Si}_4$. $\text{Li}_{12}\text{Si}_7$ is a semiconductor with an experimental gap of 0.6 eV, derived from the temperature dependence of the conductivity.³

Semiempirical tight-binding calculations were carried out on crystalline $\text{Li}_{12}\text{Si}_7$ by Böhm *et al.*^{7,8} In these calculations the crystal is split into two, electrically neutral, one-dimensional building blocks [i.e., the units $(\text{Li}_6\text{Si}_5)_\infty$ and $(\text{Li}_{12}\text{Si}_4)_\infty$ mentioned above], for which separate, one-dimensional, band structures are obtained. Böhm *et al.* find that the mechanisms involved in the stabilization of both units are different. In the case of $(\text{Li}_6\text{Si}_5)_\infty$, notwithstanding significant covalent interactions between Li and Si, essentially a Zintl-like picture applies: six Li $2s$ electrons are transferred to the Si ring, yielding an “aromatic” Si_5^{6-} cluster. The Fermi level (E_F) of this unit is in a gap between bonding and antibonding states. However, in $(\text{Li}_{12}\text{Si}_4)_\infty$ a complete transfer of Li valence charge to Si yields a unit with too much charge (Si_4^{12-}): antibonding states drop below E_F . In this case the Li acceptor levels tend to push down

the energy of the antibonding occupied states of the Si star, thus stabilizing this unit.

Another theoretical approach was, somewhat heuristically, introduced by Liebman and Vincent.^{9,10} They argue that the Si_4 unit has an “aromatic” electron arrangement with a formal charge of two electrons: one terminal Si atom is double bonded to the central Si atom and the other two terminal Si atoms obtain a charge of one electron each. In their view the chains of Si_5 units comprise a mix of Si_5^{6-} and Si_5^{2-} . To obtain overall charge neutrality they assume Li^+ and Li_3^+ cationic species.

The motivation for the present *ab initio* investigation is twofold. The previous theoretical studies were either very approximate (Liebman and Vincent) or made far-reaching assumptions concerning the electronic structure while employing a semiempirical method (Böhm *et al.*). Therefore a complete *ab initio* electronic structure calculation is desirable. This has become feasible with present-day high-speed computers and methods. Secondly, our results will allow for a comparison to the theoretical density of states of liquid $\text{Li}_{12}\text{Si}_7$,¹⁷ which was obtained with an *ab initio* method (Car-Parrinello¹¹) also. There are some minor differences between the method presently employed and the Car-Parrinello method, most importantly, the use of pseudopotentials in the latter versus a complete self-consistent treatment of the atomic cores in the former. Both methods employ density-functional theory within the local-density approximation (LDA) for exchange and correlation. We do not think that the differences are essential; the differences between our method and the semiempirical method that was employed by Böhm *et al.* are considerable, however.

This paper is organized as follows. In the next section a short description of the crystal structure is given. Section III describes the computational details. In Sec. IV the density of states of the $\text{Li}_{12}\text{Si}_7$ crystal and the isolated subunits is discussed together with a molecular-orbital model for the bond-

ing. Also a comparison with the liquid state of $\text{Li}_{12}\text{Si}_7$ is made in this section. Our conclusions are given in Sec. V.

II. STRUCTURE

Complete and well-illustrated discussions on the structure of $\text{Li}_{12}\text{Si}_7$ are given in Refs. 3, 7, and 8. We restrict ourselves to giving a short summary. The unit cell, space group 62 in the *International Tables*,¹² has the orthorhombic crystal structure with $a=8.600$, $b=19.755$, $c=14.336$ Å. The 152 atoms are ordered in two kinds of subunits. On the one hand, there are eight Li_6Si_5 units that contain a Si five ring and a staggered Li-centered Li five ring. These units are stacked on top of each other forming an infinite array in the direction of their nonperfect fivefold symmetry axis. On the other hand, there are four $\text{Li}_{12}\text{Si}_4$ structures that contain a Y-shaped Si backbone. These flat starlike Si arrangements form infinite chains that are intertwined pairwise. We will refer to these units for brevity as rings and stars, respectively. The atoms in the 22 classes occupy either Wyckoff position $8d$ or $4c$. The positional parameters we have used in our calculations are the room-temperature values from Table 3 of Ref. 3. This set of parameters resulted in a small total hydrostatic pressure of the unit cell, with individual atomic contributions of equal magnitude. This indicates that the theoretical crystal structure and positions are close to the experimental ones.

III. COMPUTATIONS

Ab initio localized-spherical-wave (LSW) band-structure calculations¹³ were performed using a scalar-relativistic Hamiltonian and including all core electrons. We used local-density exchange-correlation potentials¹⁴ inside space-filling, and therefore overlapping, spheres around the atomic constituents. It is remarkable that the structure does not need any empty spheres, atoms with zero nuclear charge, to reduce the sphere overlap. The packing of stars and rings is extremely close and does not allow for any empty spheres of reasonable size.

In the construction of the LSW basis,¹³ the spherical waves were augmented by solutions of the scalar-relativistic radial equations indicated by the atomiclike symbols $3s$, $3p$ and $2s$, $2p$ corresponding to the valence levels of the parental elements Si and Li, respectively. The internal l summation used to augment the central Hankel function at surrounding atomic sites was extended to $l=2$, resulting in the use of $3d$ orbitals for Li and Si. About 150 degrees of freedom for screening the central Hankel functions were used, resulting in screening cluster sizes varying between 38 and 40 atoms.

Iterations were performed with \mathbf{k} points lying in the centers of six tetrahedra filling an irreducible part of the first Brillouin zone. The volume per point is 1.3×10^{-6} Å³. The calculations on the complete $\text{Li}_{12}\text{Si}_7$ crystal took, on average, 145 CPU sec per iteration on a Cray C98/4256. Typically, using Broyden mixing,¹⁵ about 15 CPU min are needed to reach self-consistency. Self-consistency was assumed when the changes in the local partial charges in each atomic sphere decreased to the order of 10^{-5} . Subsequently the densities of states were obtained by a hybrid integration method¹⁶ using

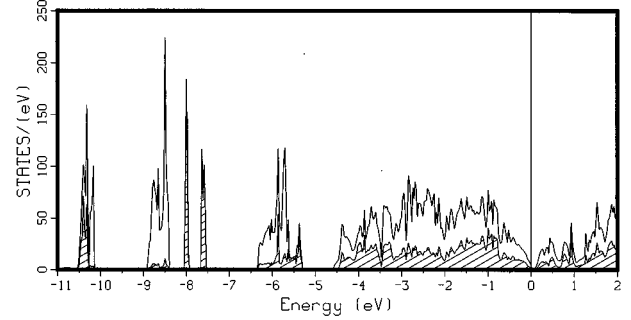


FIG. 1. The total DOS of crystalline $\text{Li}_{12}\text{Si}_7$ is given by the envelope of the curve. The shaded area indicates the contribution from the $\text{Li}_{12}\text{Si}_4$ (star) subunit. The energy scale is relative to the Fermi level E_F .

the \mathbf{k} points on the apexes and midvertices of the simplexes.

Calculations on the separate ring and star units were also carried out. Whereas Böhm *et al.*^{7,8} performed calculations on one-dimensional columns in a vacuum, we obtained the electronic structure of the isolated units by replacing the spheres of the complementary unit with empty spheres, keeping all other conditions the same.

IV. RESULTS AND DISCUSSION

A. The $\text{Li}_{12}\text{Si}_7$ crystal

The total density of states (DOS) of $\text{Li}_{12}\text{Si}_7$ is presented in Fig. 1. The DOS below -5 eV is characterized by a set of five narrow structures whereas from -5 eV to E_F there is only one broad structure. These different regions will be called regions A and B, respectively. Above E_F the DOS is similar in character to region B from which it is separated by a minimum very close to E_F . Although it may not be visible in the figure, some finite intensity remains at E_F . Analysis of the energy bands close to E_F shows that there exists a very small negative band gap. Experimentally, $\text{Li}_{12}\text{Si}_7$ is found to be a semiconductor with a gap of 0.6 eV.³ Discrepancies like these are not uncommon in LDA-based calculations as it is well known that the LDA generally tends to underestimate the band gap.

The $\text{Li}_{12}\text{Si}_4$ (star) contribution to the total DOS is indicated by the shaded curve in Fig. 1. The remaining area between the curves represents the Li_6Si_5 (ring) contribution. There is a characteristic difference between these subunits in region A, especially between -7 and -9 eV. The peak at -8.75 eV clearly originates from the ring whereas the two peaks at -8 and -7.6 eV have their highest intensity on the star. Note that some intensity for these peaks is shared between the units. Other peaks in regions A and B show some intensity differences between the ring and star DOS's but in essence they coincide. Subsequent splitting of the DOS into the total Si and total Li contributions to a subunit gives DOS figures similar to those of the total subunit. Differences between the total Li and Si curves are a matter of relative intensity that agrees with the difference in the number of valence electrons between Li and Si.

In the remaining part of this subsection the individual atom- and angular-momentum-resolved DOS curves will be briefly discussed. For more details and figures we refer to Ref. 18.

We will start with the ring. Given the symmetry of the ring and the observations made above it may be evident that the individual atomic DOS contributions are also very similar, whether of Si or Li origin. The differences that are seen have their origin outside the subunit. For instance, the decay of the -8 eV state of the star can be traced into the ring subunit, reflecting the difference in proximity between the atoms involved. Recognizing this, real differences only start appearing when the angular-momentum-resolved DOS curves are considered. Now Si, ring Li, and central Li have to be distinguished.

An individual Si contribution to the ring consists mainly of s states for each of the three peaks in region A, but there is also some p intensity which builds up with energy across this region. Region B is exclusively of p character. The difference between the partial DOS curves of a Li atom on the Li_5 ring is only a matter of relative intensity, with the p intensity slightly larger than the s intensity. This is in contrast to the central Li atom, which shows a pronounced angular momentum decomposition. For the s contribution, in the A region the peaks at -8.75 and -6 eV are completely absent, but now there is a peak at the low-energy end of the B region, centered around -3.75 eV. Also there are no p states at -6 eV. The “Si peak” at -10.3 eV actually corresponds with two peaks on the central Li atom, essentially one of s and one of p symmetry at a slightly higher energy. For region A these observations are indicative of some dispersion in the direction of the stacking axis. This evidently corresponds to an even or odd combination of the Si $3s$ states. A similar situation occurs at -8.75 eV. Around this energy the states obviously have one nodal plane going through the Si_5 ring. When for a state the nodal planes of adjacent Si rings coincide, a p -type contribution to the DOS will be found on the central Li atom. Also a d contribution occurs, which is indicative of a rotation of a nodal plane when moving along the stacking axis. Note that the pattern of region A is repeated in region B in a smeared-out fashion (a π -bonded ring and an s -bonded ring have the same level structure).

To summarize, the DOS in region A reflects the level structure of s -type orbitals on a flat five-membered ring with a fivefold rotational axis. Per Si_5 the peaks at -10.4 , -8.75 , and -6 eV should contain two, four, and four electrons, respectively. In the calculation for the isolated subunits (see below) we will, by an integration of the DOS, demonstrate that indeed these numbers are found. These facts, together with the narrowness of the peak structures, show that the DOS in region A is determined essentially by the $3s$ states of a single Si_5 ring.

Next we consider the atom and angular momentum decomposition of the DOS curve of the star unit. Projecting the star DOS into individual Si and Li contributions, the situation bears some resemblance to the ring. Region A consists of some few narrow structures whereas region B exhibits a continuous range of small peaks. The Li contribution to the DOS of the star consists of almost equal s and p contributions throughout the entire energy range. The sharp peaks in

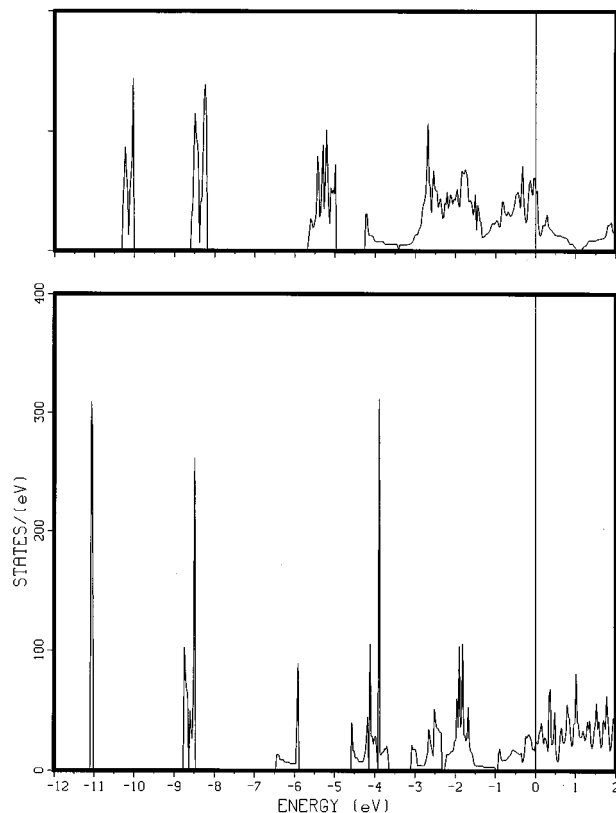


FIG. 2. Total DOS curves for the isolated $(\text{Li}_6\text{Si}_5)_\infty$ (ring) unit in the top panel and for the isolated $(\text{Li}_{12}\text{Si}_4)_\infty$ (star) unit in the bottom panel.

the A region are clearly recognized as originating from the Si atoms. They have the largest intensity on the Si atoms (almost exclusively of s character) and vary in intensity according to the position of the Si atom. The peak at about -10.5 eV has the largest contribution from the central Si. The next two peaks (-8 and -7.6 eV), considered as one split peak, originate on the outer Si atoms of the star with their intensities strongly depending on the particular Si position. Part of the peak splitting is obviously caused by the presence of the ring units. For the isolated subunit in the next section this splitting is therefore seen to be reduced. The remaining splitting is caused by the environment of the star. The Si p contributions all fall in the B region, except for the central Si atom where there is also some intensity at the double peak position. The structure around -5.5 eV consists of mainly s contributions on all the star Si atoms and exhibits significant antibonding interactions.

B. The isolated subunits

The DOS's calculated for the ring $(\text{Li}_6\text{Si}_5)_\infty$ and star $(\text{Li}_{12}\text{Si}_4)_\infty$ units are depicted in Fig. 2. We compare these curves to those of the corresponding units in the complete crystal (Fig. 1). Again we divide the DOS in the regions A (below -5 eV) and B (from -5 eV to E_F).

First the ring is considered. In the A region three peaks similar to those found in the complete crystal are seen. Of course, the tails of the complementary unit are missing now. Note also that the peaks have become shifted to higher en-

ergies. We already mentioned that this region of the DOS is mainly determined by the local arrangement of the five Si atoms. Starting at the low-energy end we find that upon integration the three peaks contain two, four, and four electrons per Si_5 ring: i.e., the level structure of s -type orbitals on a flat five-membered ring. The B region has a more pronounced shape as compared to Fig. 1. The shape of the DOS in this region is that of three overlapping peaks, extending to 1.1 eV above E_F , where a gap appears. At E_F there is no (pseudo)gap anymore. Interesting to note is that exactly two electrons per Li_6Si_5 formula unit fit into the DOS integral from E_F to the gap at 1.1 eV.

Next we move to the star unit. In region A the states of the star unit in the complete crystal, the shaded area in Fig. 1, can still be identified. In the isolated structure the peaks are sharper and the splitting of the peaks is reduced. There has also been a shift to lower energies. From low energy upwards, the peaks contain two, four, and two electrons per Si_4 star. This situation is analogous to the simple molecular orbital (MO) picture that we are going to use for the p_z orbitals of Si_4 in the next section. There are one bonding, two non-bonding, and one antibonding level per Si_4 , but now the MO's are combinations of silicon $3s$ orbitals. In region B the DOS is completely different from that of the star unit in the complete crystal. Also in this separate unit there is no gap at E_F . Instead there is a range of "gaps" in region B , notably one at -0.9 eV. From this gap to E_F the DOS contains four electrons per $\text{Li}_{12}\text{Si}_4$ unit.

From the DOS results on the isolated units it follows that a transfer of four electrons per $\text{Li}_{12}\text{Si}_4$ formula unit to two Li_6Si_5 units realizes a band gap for both subunits. The charge transfer and the change in electrostatic potential have some peak narrowing and shifting effects on the DOS in region A , but in region B the DOS is dramatically changed in both units. They differ from each other as well as from the B region DOS of Fig. 1. In fact, the agreement between the B regions of the ring and star in Fig. 1 suggests that the electron states have become delocalized to such an extent that they cannot be assigned exclusively to one of the units anymore. These considerations, in particular the charge transfer, contradict the assumption of neutral subunits as made by Böhm *et al.*^{7,8} Our calculations differ from those by Böhm *et al.* also in another aspect: we find a few sharp peaks in region A , i.e., very little dispersion, whereas they find most dispersion for low energies with bands spanning large energy intervals to a maximum of 8 eV.

C. Molecular-orbital model of the bonding

In the previous section, in particular from Fig. 2, it emerged that the occurrence of a gap in $\text{Li}_{12}\text{Si}_7$ is due to a charge transfer from the $\text{Li}_{12}\text{Si}_4$ units to the Li_6Si_5 units. In this way a gap is realized for each unit separately. Therefore the solid is best described as $[\text{Li}_{12}\text{Si}_4]^{4+}[\text{Li}_6\text{Si}_5]_2^{2-}$. In this section we present a simple model to explain the occurrence of a gap for both charged units. Both units are shown to be aromatic systems according to the Hückel $4n+2$ rule. It should be stressed that the charges in the model are formal charges representing correctly trends in the calculated results. They should not be taken literally. Also note that charges on ions are not unique and depend on the choice of basis, atomic sphere radii, etc. in any calculation.

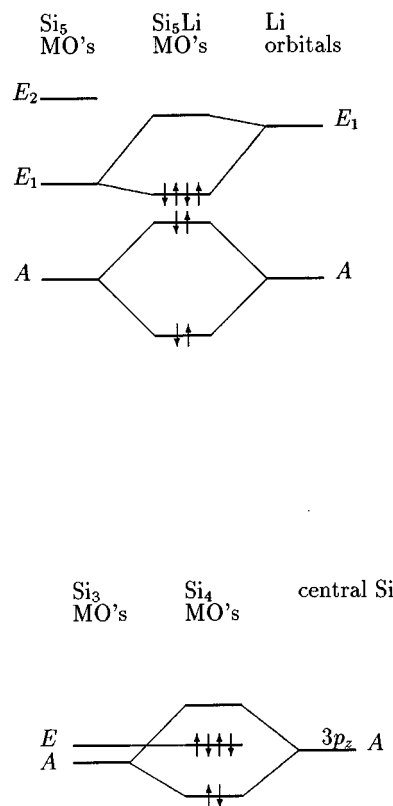


FIG. 3. Sketch of the energy-level diagram of the Si_5 ring and the central Li atom (top). Energy-level diagram of the Si_4 star (bottom).

First the basic building block of the chain of rings, $[\text{Li}_6\text{Si}_5]^{2-}$, is considered. The total number of valence electrons, including the excess charge of two electrons, is 28. Of these electrons ten reside in σ bonds between the Si atoms of the ring. Another ten electrons are assigned to lone pairs on the Si atoms of the ring. Whether these pairs constitute a covalent bonding with the Li atoms of the ring or an ionic picture applies is of no relevance to the further discussion. The p_z orbitals of the ring can accommodate six electrons, according to the Hückel rule. The remaining two electrons reside on the central Li atom. In fact, the occupied orbital of the central Li atom forms bonding and antibonding combinations with the lowest state of the aromatic π system of the Si ring. This is illustrated by a sketch of the energy-level diagram in Fig. 3. In this figure it is assumed that the unit has a perfect fivefold rotational symmetry so that the levels can be classified according to the group C_5 . The somewhat surprising result, a negatively charged Li atom, also appears from the calculation of the neutral $(\text{Li}_6\text{Si}_5)_\infty$ crystal, where the central Li atom has an excess charge of "0.9" electrons. In the full crystal this charge is actually reduced by interactions between rings and stars.

For the $[\text{Li}_{12}\text{Si}_4]^{4+}$ unit the valence electron count, after four electrons have been transferred to the ring units, is 24. There are six electrons forming three σ bonds between the central Si atom and the outer Si atoms of the star. Another 12 electrons can be assigned to six lone pairs on the outer Si atoms (or, in covalent language, these form bonds with the

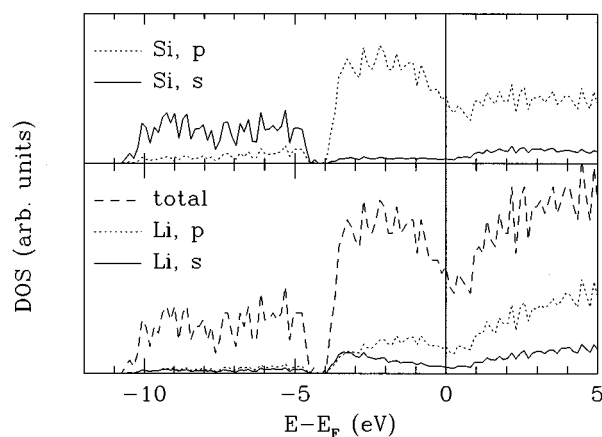


FIG. 4. The liquid state DOS of $\text{Li}_{12}\text{Si}_7$ and its decomposition into elemental and orbital momentum contributions.

Li atoms). The remaining six electrons reside in the p_z orbitals, again fulfilling the Hückel rule. Figure 3 shows a sketch of the energy levels of the π system. In classifying the levels according to the group C_3 , a perfect threefold rotational axis is assumed. The gap is in between the E MO's of the outer three Si atoms and the antibonding combination of the Si_3 A MO and the $3p_z$ orbital of the central Si atom.

In the real solid the interactions between the star and ring units lead to a broadening of energy levels, but the semiconducting properties persist. At lower energies the separate peaks, of primarily Si $3s$ character, remain the dominant feature of the DOS. This is not in disagreement with the simple picture outlined above. It demonstrates that s - p hybridization on Si plays a minor role only.

D. Comparison with the liquid state

The DOS of liquid $\text{Li}_{12}\text{Si}_7$ and its angular momentum decomposition (Fig. 4) were obtained earlier¹⁷ using the Car-Parrinello method. The DOS is calculated in a simple cubic box containing 35 Si and 60 Li atoms and refers to the Γ point only. As a consequence the DOS contains considerable noise.

Just as for the solid two different regions can be discerned in the liquid state DOS. The lowest-lying structure is predominantly of Si s character and has a width of about 6 eV

(region A). The other structure (region B) begins at about -4.2 eV below E_F and intersects the Fermi level. In this region the states are mainly of p character on Si, while for Li a considerable mixing of s and p occurs. The major separation of states that was found for the solid can therefore still be recognized in the liquid. In the crystal the symmetry of the Si rings and stars is responsible for the occurrence of only a few peaks in the A region. Of course in the liquid state the symmetry of the crystal is lost, giving a broad "band" of states. However, the distribution of the angles between the Si bonds exhibits a large peak around 110° . A minor peak at 60° is also observed. Note the similarity with the bond angles in the crystal: 108° for the ring and 120° for the star. On comparing the B regions a striking similarity between the DOS of the solid and that of the liquid is observed.

V. CONCLUSION

We have found that the DOS of $\text{Li}_{12}\text{Si}_7$ can be split into two regions. The DOS in the region below -5 eV is clearly dominated by the local arrangement of Si atoms. Using calculations on the isolated units it was shown that a transfer of charge moves the Fermi level into a gap on both units. A molecular-orbital model based on this charge transfer and the local arrangement of the atoms, i.e., the Si_4 star and the Si_5 ring sandwiched between Li atoms, explains the occurrence of the gaps on both subunits. Our description of the electronic structure differs from both that by Böhm *et al.*^{7,8} and that by Liebman and Vincent.^{9,10} It is similar to a first attempt by von Schnering *et al.*⁵ to provide a model in terms of formal ions: $\text{Li}_{24}^+[\text{Si}_4]^{8-}[\text{Si}_5]_2^{8-}$. The essential difference is that in our model two electrons less reside on the Si_5 ring where a Li atom opposite the plane of the silicon ring has its $2s$ shell filled.

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